Multiscale Modelling of Two-dimensional Materials for Solar Water Splitting and Hydrogen Storage

Executive Summary of Thesis

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Table of Contents

Definition of the Problem:

In recent years, the world has witnessed a surge in energy demands driven by technological advancements and rapid population growth.[1] This, coupled with decline of traditional fossil fuel such as petrol, diesel, etc., has necessitated the search for alternative fuels, particularly in the transportation sector.[2] One promising candidate that has garnered significant attention is hydrogen fuel which possesses several desirable characteristics making it an attractive alternative to conventional fuels.[3] Firstly, it is abundantly available, with sources ranging from water to biomass and renewable energy resources.[3] Unlike fossil fuels, hydrogen is considered eco-friendly since it produces only water and heat when used as a fuel, avoiding harmful emissions such as greenhouse gases.[3] Additionally, hydrogen boasts a high energy density, meaning it can store and deliver more energy per unit of mass in comparison to alternative fuels.[4] However, the practical use of hydrogen fuel faces two main challenges: efficient and cost-effective production and compact storage.[5–7] This thesis addresses these challenges by designing advanced two-dimensional (2D) nanomaterials to produce hydrogen through water splitting, as well as exploring efficient method for hydrogen storage.[5–7]

Computational Methodology:

In this thesis, an exploration of structural, electronic, adsorption and catalytic properties was conducted utilizing first-principles-based density functional theory (DFT) through Quantum ESPRESSO software.[8] The exchange-correlation interaction was treated using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA).[9] The correction of long-range interactions has been achieved by implementing the Grimme-D2 (or D3) correction.[10] To accurately represent the 2D nature of the material, sufficient vacuum was added perpendicular to the plane of the monolayer as per requirement. This modification successfully eliminated any interactions between the periodic images, ensuring an accurate simulation. To obtain the relaxed configuration for each considered structure, an iterative convergence process was employed until the maximum Hellmann-Feynman force acting on each atom reached a value lower than 10^{-3} eV/Å. In this thesis work, all the pictorial representations of structures charge density differences were prepared by the XCrySDen[11] and Vesta[12] visualization packages.

Summary and Key Findings:

Our study delves into hydrogen evolution reaction (HER) activity of pristine α-SiX (X=N, P, As, Sb, Bi), Ni anchored α-SiX (X=N, P, As, Sb, Bi) single-atom catalysts (SACs), pristine holey graphyne (HGY) and transition metals (Zr, Y, V, Sc, Mn, Co, Fe, Cr) anchored HGY SACs.[13,14] This investigation is carried out through comprehensive dispersion corrected DFT simulations. Our results for the Gibbs free energy of H adsorption (ΔG_H) suggest that pristine form of α-SiX (X = N, P, As, Sb, Bi) and HGY monolayers are ineffective as catalysts for the HER activity. To enhance the HER activity, we have implemented a strategy of anchoring transition metals onto α-SiX (where X = N, P, As, Sb, Bi) and HGY monolayers in order to create SACs. Furthermore, we elucidate the alterations in the structural and electronic properties of α-SiX (X=N, P, As, Sb, Bi) and HGY monolayers due to anchoring with transition metals. This is achieved by considering orbital interactions, changes in band structures and partial density of states (PDOS) analysis. The significant bonding between Ni metal and α-SiX (X = N, P, As, Sb, Bi) monolayers, as well as between transition metals and HGY monolayer, facilitated by p-d hybridization, enhances reactivity and conductivity. This is further attributed to a decrease in the band gap of the semiconducting α-SiX and HGY monolayers. Our DFT finding predicts that Ni@α-SiX and Cr@HGY SACs emerge as highly efficient catalysts for HER, exhibiting remarkably low ΔG_H values of -0.04 eV and -0.05 eV, respectively. To validate their stability, we conducted extensive ab initio molecular dynamics (AIMD) simulations at 300K, affirming the integrity of Ni@α-SiX and Cr@HGY SACs at room temperature. Given the exceptional electrochemical performance for HER activity and stability of Ni@α-SiX and Cr@HGY SACs, they hold promise as viable catalysts for hydrogen production through the HER activity.

The dispersion corrected DFT simulations on pristine 2D orthorhombic diboron dinitride (o-B_2N_2) for HER activity show its limited suitability as a catalyst, as inferred from the ΔG_H calculation.[15] However, the introduction of vacancy defects induces significant changes in the monolayer's structure and electronic properties, leading to the widening of the band gap from 0.66 eV to 0.99 eV in the case of the BN vacancy. Remarkably, the BN defected configuration exhibits ΔG_H close to zero compared to B and N defected as well as pristine configurations. This BN defect augmented HER activity by 77.34% in comparison to the pristine configuration at pH = 0. With the inclusion of C doping, the system's behavior transformed from a semiconductor to a metal. The ΔG_H of the C doped 2D o-B_2N_2 approached zero in both scenarios, signifying its suitability for HER. The C doping resulted in 86.71% boost in HER activity at the B site and 83.59% enhancement at the N site relative to the pristine configuration at pH = 0. This improvement was attributed to altered charge distribution following defect creation and C doping. Consequently, our findings propose that the metallic C doped 2D o-B_2N_2 could effectively act as an "electrocatalysts" for the HER activity within the pH range of 0 to 7. On the other hand, the BN defected 2D o-B_2N_2, characterized by 0.99 eV band gap, displays potential as a "photocatalyst" for HER activity at pH = 0. In addition, through AIMD simulations conducted at 300K, the structural integrity of 2D o-B_2N_2 with BN defects and C doping at room temperature is confirmed.

We explored the possibility of the pristine, defected and metals (including Na and K alkali metals; Be, Mg and Ca alkaline-earth metals and Sc, Ti, Y and Zr transition metals) decorated 2D o-B_2N_2 as a hydrogen storage medium through dispersion corrected DFT calculations.[16] The findings indicate that the pristine, defected and metals Na, K, Be, Mg, Ca, Sc, Y and Zr decorated 2D o-B_2N_2 did not align favourably with the U.S. Department of Energy (DoE) requirements for an effective hydrogen storage medium. Nonetheless, promising results emerged from the Ti decorated 2D o-B_2N_2, suggesting its suitability as a hydrogen storage medium. Notably, the Ti atoms exhibited a strong and favourable bonding with the 2D o-B_2N_2, leading to a decrement in the band gap and an increase in conductivity. The adsorption energy for first hydrogen on the Ti decorated 2D o-B_2N_2 is -0.47 eV, satisfying the DoE's criteria. Furthermore, the charge donation from the Ti atom to the 2D o-B_2N_2 was observed through PDOS and Löwdin charge analysis. The two Ti decorated configuration demonstrated the capacity to bind a total of thirty-four hydrogen molecules, with average adsorption energy of -0.31 eV/H_2 and 396 K of desorption temperature. The calculated gravimetric storage capacity is 11.21%, notably surpassing the DoE's specified range. At a temperature of 396 K, our AIMD results convincingly demonstrate the excellent thermal stability of the Ti decorated 2D o-B_2N_2. As a summary, this research highlights the promising prospects of the Ti decorated 2D o-B_2N_2 as an efficient medium for high-capacity hydrogen storage.

Future Prospects:

In this section, we will briefly discuss few future prospects. In connection with this thesis, the studied materials have not been examined under conditions such as strain (both expansive and compressive)[17], transition metals (which are not addressed in the current thesis)[18] decoration or substitutional doping[19] for applications in hydrogen production through water splitting and hydrogen storage medium.[20,21] Moreover, a separate study could be conducted to predict the formation of various 2D allotropes of the studied materials by altering their chemical composition.[22] This inspiration can be drawn from a thorough literature survey and state-of-the-art DFT simulations can be employed for this purpose. Exploring the landscape of 2D allotropes can uncover novel structures with distinct properties, potentially unlocking new avenues for applications beyond what is currently understood. In addition to the aforementioned aspects, the stable 2D materials that were examined within the scope of this thesis possess the potential to be further investigated for a diverse array of energy-related applications, such as solar cells and thermoelectric devices.[23–25] Furthermore, their applicability extends to various other fields, including but not limited to bio-sensors and toxic gas sensors.[26–28] The unique surface-to-volume ratio and high surface reactivity of 2D materials can enable highly sensitive and selective sensing platforms, revolutionizing the detection of biological molecules and hazardous gases.[26–28] Beyond sensing applications, these materials could find utility in batteries and catalytic applications.[29,30] Their high surface area and tailored electronic properties can contribute to improved energy storage and conversion, as well as catalytic processes like the oxygen evolution and oxygen reduction reactions in fuel cells.[31–33] Hence, we hope that our theoretical data will serve as inspiration for experimentalists who aim to create cost-effective, high-performance HER catalysts for water-splitting and to design suitable materials for hydrogen storage applications. The integration of our insights with experimental efforts has the potential to drive innovation in the fields of renewable energy.

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